

## CD221. LECTURE 4. FUNDAMENTAL RELATIONS. SOLVING THE BASIC PROBLEM OF THERMODYNAMICS

By assuming that a quantity called the entropy underlies the tendency for simple systems (characterized in equilibrium by  $U$ ,  $V$  and  $N$ ) to become maximally uniform following the release of an internal constraint, we can assert that

$$S = S(U, V, N) \quad (1)$$

This expression is the central relation of *thermodynamics*. Because  $U$ ,  $V$  and  $N$  have been assumed (in Postulate I) to completely characterize the equilibrium state of a system, and because  $S$ , also by assumption (Postulate II), completely controls the evolution of the system from one state to another, the above relation in effect tells us everything we can know thermodynamically about the system. For this reason, it is called a fundamental relation.

Knowledge of a system's fundamental relation guarantees complete knowledge of all its thermodynamic attributes, as we'll see later.

One of the tasks of statistical thermodynamics will be to find the precise form of the fundamental relation for a given system.

Because of Postulate III, we can uniquely invert Eq. (1) as

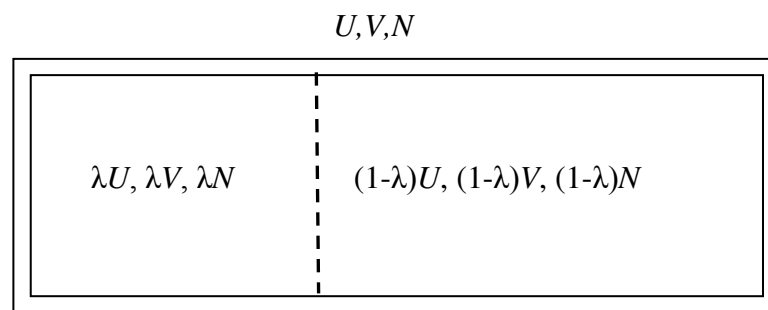
$$U = U(S, V, N) \quad (2)$$

Eq. (2) must also be a fundamental relation because it has the same information content as Eq. (1). Eq. (2) is referred to as a fundamental relation in the energy representation, while Eq. (1) is referred to as a fundamental relation in the entropy representation.

### • Some other implications

The additivity property of  $S$  in Postulate III also allows us to infer that  $S$  is an extensive property of a system, i.e., that it increases in direct proportion to system size.

To show this, consider a simple system with energy  $U$ , volume  $V$  and number of moles  $N$ . Imagine partitioning it *mentally* into two parts, in some arbitrary ratio, such that a parameter  $\lambda$  describes the fraction that each part is of the whole. (If the ratio were 1:1, for instance,  $\lambda$  would be 1/2; if it were 1:2,  $\lambda$  would be 1/3; and so on.) Schematically, the system would look like this:



This partitioning of the system leads to the following obvious relations:

$$U = \lambda U + (1 - \lambda)U \quad (3a)$$

$$V = \lambda V + (1 - \lambda)V \quad (3b)$$

$$N = \lambda N + (1 - \lambda)N \quad (3c)$$

Each of the imaginary sub-systems has an entropy associated with it, the sub-system entropies being functions, respectively, of  $(\lambda U, \lambda V, \lambda N)$  and of  $((1 - \lambda)U, (1 - \lambda)V, (1 - \lambda)N)$ . By the additivity property of the entropy we can write for the composite system that

$$S(U, V, N) = S(\lambda U, \lambda V, \lambda N) + S((1 - \lambda)U, (1 - \lambda)V, (1 - \lambda)N) \quad (4)$$

Eq. (4) can be put in the form  $S = \lambda S + (1 - \lambda)S$  [cf. Eqs. (3a)-(3c)] only if it is the case that

$$S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N) \quad (5a)$$

and

$$S((1 - \lambda)U, (1 - \lambda)V, (1 - \lambda)N) = (1 - \lambda)S(U, V, N) \quad (5b)$$

Since  $\lambda$  is arbitrary (but is restricted to lying between 0 and 1) Eqs. (5a) and (5b) imply, more generally, that

$$S(\alpha U, \alpha V, \alpha N) = \alpha S(U, V, N), \quad 0 < \alpha < 1 \quad (6)$$

where  $\alpha$  is some scaling parameter.

It's possible to show that the scaling relation of Eq. (6) isn't restricted to  $\alpha$  values in the indicated range. To do this, start by writing Eq. (6) as

$$\alpha S(U, V, N) = S(\alpha U, \alpha V, \alpha N) \quad (7)$$

and then identically as

$$\alpha S\left(\frac{1}{\alpha} \alpha U, \frac{1}{\alpha} \alpha V, \frac{1}{\alpha} \alpha N\right) = S(\alpha U, \alpha V, \alpha N) \quad (8)$$

If we now define the new variables  $U' = \alpha U, V' = \alpha V$  and  $N' = \alpha N$ , along with the new variable  $\lambda' = 1/\alpha$ , and substitute these variables into Eq. (8), we get

$$\frac{1}{\lambda'} S(\lambda' U', \lambda' V', \lambda' N') = S(U', V', N') \quad (9)$$

or, rearranging,

$$S(\lambda'U', \lambda'V', \lambda'N') = \lambda'S(U', V', N'), \quad \lambda' > 0 \quad (10)$$

Since the symbols we've used in Eq. (10) are just “dummy” variables, we can write the equation equivalently as

$$S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N), \quad \lambda > 0 \quad (11)$$

This is the defining equation of an extensive quantity – it says that the entropy increases (or decreases, since  $\lambda$  can be less than 1) in direct proportion to the increase (or decrease) in the variables that it depends on.

• Molar quantities

Although  $N$  has so far been defined as the number of particles in a system, there's no loss of generality in thinking of it as the number of moles. If we now interpret  $N$  in the above equations in this way, then using Eq. (11), we can introduce the notion of “molar” quantities. Let  $\lambda = 1/N$  in this equation. It then follows that

$$S(U/N, V/N, 1) = N^{-1}S(U, V, N) \quad (12)$$

Here,  $U/N$  and  $V/N$  obviously define what we can call the molar energy and the molar volume of a substance, i.e., the energy and volume *per mole* of that substance. It's convenient to introduce the notation  $u = U/N$  and  $v = V/N$ . Then Eq. (12) becomes

$$S(u, v, 1) = N^{-1}S(U, V, N) \quad (13)$$

The LHS of this equation is clearly the entropy of 1 mole of the substance – which means that it is actually the molar entropy of the substance, and therefore, in the notation introduced above, it can be written as  $s$ . So Eq. (13) becomes

$$s(u, v) = N^{-1}S(U, V, N)$$

or, rearranging,

$$S(U, V, N) = Ns(u, v) \quad (14)$$

which is simply the statement that the entropy of  $N$  moles of something is  $N$  times its molar entropy.

Postulates I, II and III are actually sufficient to solve the fundamental problem of thermodynamics, but Callen introduces a fourth postulate that for now we'll simply state:

**Postulate IV. The entropy of any system vanishes in the state for which  $(\partial U / \partial S)_{V,N} = 0$ .**

While all these postulates (except perhaps the fourth) may seem plausible, do they in fact tell us how to solve the fundamental problem of thermodynamics? It's to this problem and its solution that we shall turn next. Before we do so, we'll need to first review some results from elementary calculus.

• Making small changes: Differential calculus

Thermodynamics is concerned, in general, with the consequences of small changes. This is mostly because large changes can often be calculated by adding up or integrating the effects of many small changes. At the same time, a lot of questions of experimental interest really do involve only small changes.

The natural language of small changes is differential calculus, where these changes are represented as differentials. A few results from differential calculus are worth recalling at this point. It is particularly important to recall that if a function  $f$  depends on some variable  $x$ , such that  $f = f(x)$ , then when  $x$  is changed to  $x + dx$  (where  $dx$  is a tiny bit of  $x$  called the differential of  $x$ ), the new value of  $f$ , viz.,  $f(x + dx)$ , can be represented as a Taylor's series expansion in powers of  $dx$ . This expansion takes the form

$$f(x + dx) = f(x) + \frac{df(x)}{dx} dx + \frac{1}{2!} \frac{d^2 f(x)}{dx^2} (dx)^2 + \frac{1}{3!} \frac{d^3 f(x)}{dx^3} (dx)^3 + \dots \quad (15)$$

which can be rearranged to

$$f(x + dx) - f(x) = \frac{df(x)}{dx} dx + \frac{1}{2!} \frac{d^2 f(x)}{dx^2} (dx)^2 + \frac{1}{3!} \frac{d^3 f(x)}{dx^3} (dx)^3 + \dots \quad (16)$$

With the definitions  $\Delta f = f(x + dx) - f(x)$ ,  $df = (df / dx) dx$ ,  $d^2 f = (d^2 f / dx^2) (dx)^2$  and  $d^3 f = (d^3 f / dx^3) (dx)^3$ , Eq. (16) becomes

$$\Delta f = df + \frac{1}{2!} d^2 f + \frac{1}{3!} d^3 f + \dots \quad (17)$$

The quantity  $df$  is called the first differential of  $f$ ,  $d^2 f$  is called the second differential of  $f$ ,  $d^3 f$  is called the third differential of  $f$ , and so on. For truly infinitesimal values of  $dx$ , it's a very good approximation to represent  $\Delta f$  by just the first term in Eq. (17), which means that  $\Delta f \approx df = (df / dx) dx$ .

Thermodynamics typically deals with functions that depend on a number of variables (3 in the examples we'll consider in this course), and the generalization of Eq. (16) that will be relevant to such three-variable functions is shown below:

$$f(x + dx, y + dy, z + dz) - f(x, y, z) \equiv \Delta f = df + \frac{1}{2!} d^2 f + \frac{1}{3!} d^3 f + \dots \quad (18a)$$

where

$$df = \left( \frac{\partial f}{\partial x} \right)_{y,z} dx + \left( \frac{\partial f}{\partial y} \right)_{x,z} dy + \left( \frac{\partial f}{\partial z} \right)_{x,y} dz \quad (18b)$$

and

$$\begin{aligned} d^2 f = & \left( \frac{\partial^2 f}{\partial x^2} \right)_{y,z} (dx)^2 + \left( \frac{\partial^2 f}{\partial y^2} \right)_{x,z} (dy)^2 + \left( \frac{\partial^2 f}{\partial z^2} \right)_{x,y} (dz)^2 + 2 \frac{\partial^2 f}{\partial x \partial y} dx dy + \\ & + 2 \frac{\partial^2 f}{\partial x \partial z} dx dz + 2 \frac{\partial^2 f}{\partial y \partial z} dy dz \end{aligned} \quad (18c)$$

(For the moment it won't be necessary to provide the expression for  $d^3 f$  or other higher order terms.)

If it happens that  $\Delta f$  in Eq. (18a) is produced by a change in, say,  $x$  at constant values of  $y$  and  $z$  (such that  $dy$  and  $dz$  are 0), and if the change *extremizes*  $f$  (i.e., maximizes or minimizes it), then  $df$  in Eq. (18b) is 0, because  $(\partial f / \partial x)_{y,z}$ , the slope of  $f$ , vanishes. At the same time,  $d^2 f$  in Eq. (18c), which is given by just the first term on the right hand side of the equation, becomes either positive or negative; it is positive if  $f$  is at a minimum (because  $(\partial^2 f / \partial x^2)_{y,z} > 0$ ), and it is negative if  $f$  is at a maximum (because  $(\partial^2 f / \partial x^2)_{y,z} < 0$ .) These results are worth bearing in mind when we turn our attention to thermodynamics.

#### • Application to thermodynamics

In finding a solution to the fundamental problem of thermodynamics, it's useful to start with the expression for the fundamental relation of a system in the energy representation, which in general takes the form

$$U = U(S, V, N) \quad (19)$$

If small changes are made to  $S$ ,  $V$  and  $N$ , the change in  $U$  is given by

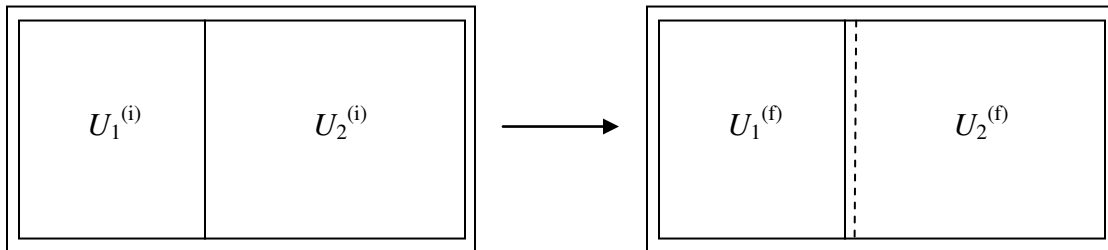
$$dU = \left( \frac{\partial U}{\partial S} \right)_{V,N} dS + \left( \frac{\partial U}{\partial V} \right)_{S,N} dV + \left( \frac{\partial U}{\partial N} \right)_{S,V} dN \quad (20)$$

Let's assign special symbols to the partial derivatives that appear in this equation; specifically, let  $(\partial U / \partial S)_{V,N} \equiv T$ ,  $(\partial U / \partial V)_{S,N} \equiv -P$  and  $(\partial U / \partial N)_{S,V} \equiv \mu$ . Eq. (20) then becomes

$$dU = TdS - PdV + \mu dN \quad (21)$$

It should be evident that  $T$ ,  $P$  and  $\mu$  are themselves functions of  $S$ ,  $V$  and  $N$ . That is, in general  $T = T(S, V, N)$ ,  $P = P(S, V, N)$  and  $\mu = \mu(S, V, N)$ . Each of these relations is called an *equation of state*, and knowledge of all three (and not just one or two) is equivalent to knowing the fundamental equation itself. (Why this is so will hopefully become clear later.) Furthermore, because  $T$ ,  $P$  and  $\mu$  are ratios of two extensive quantities, they are unaffected by any changes that may be made to the variables they depend on. Such quantities are called *intensive*.

Although you've encountered Eq. (21) before, and probably know full well its thermodynamic significance, we'll see if we can discover its physical content from what it tells us about a closed composite system whose internal constraint is made diathermal (but *not* moveable or permeable.) In the course of such a change, the system evolves from one macrostate to another, these states being characterized by particular values of the energy, as depicted below:



Here the subscripts  $i$  and  $f$  stand for initial and final, respectively, and the vertical dashed line on the right is meant to suggest that the internal constraint permits thermal interactions between the two sub-systems, while remaining rigid and impermeable. Only the energy is needed to specify the state of each sub-system completely since  $V$  and  $N$  have been assumed to remain fixed during the change. It's further assumed that  $U_1^{(i)}$  and  $U_2^{(i)}$  are known (meaning, they have somehow been independently measured), and that their sum,  $U_1^{(i)} + U_2^{(i)}$ , has some definite value  $U$ , which is a constant because the composite system is closed. But we don't know the energies  $U_1^{(f)}$  and  $U_2^{(f)}$  of the sub-systems in the final state, and finding them is what we need to do to solve the fundamental problem of thermodynamics. Can we determine these unknowns from our postulates? We already know one equation that relates them, viz.,

$$U_1^{(f)} + U_2^{(f)} = U \quad (22)$$

and if we knew one more, we'd have two equations in two unknowns, making it possible to determine their values.

From our postulates, we know that in the final state, the composite system has an entropy  $S^{(f)}$  that is the sum of the entropies of 1 and 2. That is,

$$S^{(f)} = S_1^{(f)} + S_2^{(f)} \quad (23)$$

Because the entropy has been extremized during the change (again by our postulate),  $dS^{(f)} = 0$ , and so

$$dS_1^{(f)} = -dS_2^{(f)} \quad (24)$$

Further, since the entropies of 1 and 2 are functions of  $U_1^{(f)}$  and  $U_2^{(f)}$ , we can use the Taylor's expansions of the preceding section to write

$$dS_1^{(f)} = \left( \frac{\partial S_1^{(f)}}{\partial U_1^{(f)}} \right) dU_1^{(f)} \quad (25a)$$

and

$$dS_2^{(f)} = \left( \frac{\partial S_2^{(f)}}{\partial U_2^{(f)}} \right) dU_2^{(f)} \quad (25b)$$

From the definition of the parameter  $T$  given earlier, it's clear that the partial derivatives in Eqs. (25a) and (25b) are just reciprocals of  $T$ . These equations can therefore be written

$$dS_1^{(f)} = \frac{1}{T_1^{(f)}} dU_1^{(f)} \quad (26a)$$

and

$$dS_2^{(f)} = \frac{1}{T_2^{(f)}} dU_2^{(f)} \quad (26b)$$

Substituting Eqs. (26a) and (26b) into Eq. (24), we get

$$\frac{1}{T_1^{(f)}} dU_1^{(f)} = -\frac{1}{T_2^{(f)}} dU_2^{(f)} \quad (27)$$

By the conservation of energy (as contained in the fact that the composite system is closed), the gain or loss of energy in 2 must come entirely from the loss or gain of energy in 1, which means that  $dU_1^{(f)} = -dU_2^{(f)}$ . If this result is plugged into (27), we finally arrive at

$$T_1^{(f)} = T_2^{(f)} \quad (28)$$

But since  $T$  itself is a function of  $U$  in general (though we don't know the precise form of the functional relationship), Eq. (28) is actually an equation in  $U_1^{(f)}$  and  $U_2^{(f)}$ , and this therefore is the second equation in these two unknowns that we were looking for. Together with Eq. (22), it completely determines the values of the unknowns, and hence solves the thermodynamic problem.